Visible light induced controlled cationic polymerization by in-situ generated catalyst from manganese carbonyl

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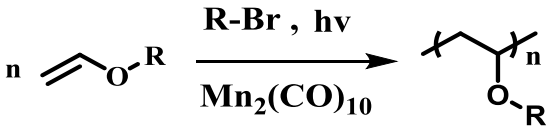
ABSTRACT: A robust method for preparing controlled poly(vinyl ethers) utilizing commercially available reagents under visible light is reported. Pentacarbonylbromomanganese ($Mn(CO)_5Br$), generated from the conventional photolysis of manganese carbonyl and halide abstraction, is considered as a catalyst to oxidize carbon radical to carbenium ion in this polymerization. Polymerization behavior including the effects of solvents and monomers have been investigated. The polymers prepared by this method are characterized by nuclear magnetic resonance (NMR), size exclusion chromatography (SEC) and matrix assisted laser desorption/ionization time of flight mass spectroscopy (MALDI TOF MS). Furthermore, polymers with multimodal distributions are prepared by regulating the irradiation time of the light source.

Controlled polymerization has revolutionized the preparation of polymers in recent years. Living anionic polymerization, first reported in 1956[1], paved the way to controlled polymerization techniques, which now also include living cationic polymerization[2] and controlled radical polymerization (CRP), e.g. nitroxide mediated polymerization (NMP)[3], atom-transfer radical polymerization (ATRP)[4] and reversible addition-fragmentation chain transfer (RAFT)[5] polymerization. These methods are complementary as they employ different types of monomers. Indeed, cationic polymerization typically employs vinyl ethers, owing to their electron-donating alkoxy group. Living cationic polymerization was first reported in 1980s by Higashimura et al. and Kennedy et al. who polymerised vinyl ehters[6] and isobutene[7]. Following these initial reports, various systems were develpped for living cationic polymerization, mainly through reversible and transient activation of dormant carbon–halogen or oxygen–ester bonds to carbocationic species using metal-based Lewis acid catalysts (MXn)[8]. This mechanism was recently extended to ATRP. Following a similar idea, the concept of RAFT polymerization has been extended to cationic RAFT polymerization utilizing a cationic RAFT agent[9]. Both of these methods are carried out with a specifically synthesized agents (HCI-IBVE adduct or cationic RAFT agents), which is key to generate "dormant" species aiding to suppress uncontrolled side reactions (isomerizations, hydride abstraction and transfer reactions) by stabilizing carbenium ions in cationic polymerization.[10] These systems require the reagents to be purified since the polymerization is very sensitive to impurities and traces of water. Recent advance in the polymerization process has seen the use of visible light to mediate the reaction. Light activation enables reactions to be performed at room temperature, require low energy, cheap commercial light sources, and allows for spatial and temporal control of the polymerisation.[11] Hawker and co-workers have reported $Ir(ppy)_3$-based system for photo-ATRP[12] and Boyer and co-workers extended this photocatalytic system to conventional RAFT polymerization, coined PET-RAFT[13]. Photo-RAFT utilizing direct photolysis of RAFT agent[14] under visible light and Cu(1) species in photo-ATRP[15] were also developed for the preparation of well-defined polymers. Further recent developments have seen the use of metals[16] and organo-catalysts[17] for controlled polymerization under different light wavelength[18] and even without deoxygeneration[19]. Furthermore, these photo-CRP are widely applied for polymerization induce self-assembly (PISA)[20] and the synthesis of sequence controlled polymers[21].

Very recently, photo-induced controlled cationic polymerization has been reported utilizing a combination of cationic

RAFT agent and conventional light sensitive onium salt[22]. Yagic and co-workers reported a PRORD process for controlled cationic polymerization of IBVE[23]. Nicewicz and coworkers reported a visible light induced metal-free controlled cationic polymerization of pMOS[24]. Among the catalysts available for visible light mediate reactions, organic halides and manganese carbonyl are known to generate radicals under visible light through halide abstraction[25]. This reaction has been used in various polymerization process. For instance, Kamigaito and coworkers apply this approach in RAFT polymerization[26] and degenerative iodine-transfer polymerization[27] to generate the initiating radicals, whilst Yagci and coworkers used it both in radical polymerization[28] and cationic polymerization[29]. In these systems, an onium salt is necessary for electron transfer from the generated radicals to form a carbenium ions. Another product from the halide abstraction, $Mn(CO)_5Br$, is usually recognized as a stable compound in these polymerization. However, we hypothesised that this compound acts as oxidant and can directly oxidize proper carbon radicals to carbenium ions. Herein, we report our investigation of this system by studying a controlled cationic polymerization of vinyl ethers, utilizing a catalyst generated *in-situ* under visible light from commercially available reagents (Scheme 1). Interestingly, reagents in this system do not need extra purification, which simplifies the operation the usually stringent process of cationic polymerization.



Scheme 1. Visible light induced cationic polymerization of vinyl ethers.

The polymerization was initially performed with various organic halides and isobutyl vinyl ether (IBVE), see Table S1. Narrow molecular weight distribution was observed in the polymerization with ethyl 2-bromopropanoate (EBP) (Entry 4, Table S1), showing the structure of the organic halides promotes control over polymerization. The polymerization rate was found to decrease as the amount of $Mn_2(CO)_{10}$, is reduced (Table 1, entries 1-5), whilst the molecular weight determined by SEC ($M_{n,SEC}$) matches predicted values ($M_{n,th}$), thus suggesting that $Mn_2(CO)_{10}$ acts as a catalyst in this polymerization. However, $M_{n,SEC}$ increases over $M_{n,th}$ and the molecular weight distribution broadens up when the amount of $Mn_2(CO)_{10}$ is decreased below 0.1 molar ratio of EBP (Entry 4-5, Table 1), possibly due to side reactions. On the other hand, increasing the amount of $Mn_2(CO)_{10}$ to 0.5 molar ratio of EBP (Entry 1) also leads to a broader molecular weight distribution, possibly caused by fast polymerization and further side reactions. However, at the optimal ratio EBP / $Mn_2(CO)_{10}$ of 0.2, it is possible to target specific molecular weights with reasonably good accuracy (Entry 6-7, Table 1). It is also noteworthy that control experiments in absence of EBP or $Mn_2(CO)_{10}$ or light led to no polymerization (Entry 8-10, Table 1). To verify that the presence of water and KOH in the commercially available monomer have no effect on this polymerisation, IBVE was also purified and polymerized (Table 1, entry 11), showing no obvious difference from the polymerization utilizing the unpurified monomer, although the polymerization rate was slightly higher.

Table 1. Polymerization of IBVE under various conditions at 0 °C with blue LED, V_M = 0.5mL

Entry	[M]/[EBP]/ [$Mn_2(CO)_{10}$]	Time	Conv.%	[a]$M_{n,th}$ (g/mol)	[b]$M_{n,SEC}$ (g/mol)	$Đ$
1	200:1:0.5	6 min	73.5	14700	16700	1.47
2	200:1:0.2	14 min	71.6	14500	15900	1.18
3	200:1:0.1	15 min	71.3	14300	18100	1.15
4	200:1:0.05	75 min	81.4	16500	36100	1.34
5	200:1:0.01	38 h	34.6	7100	37800	1.89
6	100:1:0.2	5 min	81.8	8200	11600	1.41
7	500:1:0.2	50min	58.7	29400	32400	1.46
8	200:1:0	5 h	-	-	-	-
9	200:0:0.2	5 h	-	-	-	-
[c] 10	200:1:0.2	5 h	-	-	-	-
[d] 11	200:1:0.2	14 min	93.1	18800	17200	1.28
[e] 12	200:1:0.2	5 min	90.3	18300	17800	1.22
[f] 13	200:1:0.2	5 h	58.3	11900	20500	1.78

a) Calculated based on conversion ($M_{n,th}$ = $[M]_0/[EBP]_0$ × conversion × M + M_{EBP}); b) Determined by SEC using polystyrene (PS) as standard in tetrahydrofuran (THF); c) In the dark; d) With purified monomer; e) At 25 °C; f) At 0 °C

The effect of temperature was also investigated and it was found that the polymerization rate increases when increasing temperature to 25 °C, whilst a slower polymerization rate is observed at - 25 °C, with broader molecular weight distribution.

Toluene, dichloromethane (DCM) and hexane are typically used as solvents for cationic polymerization, whilst ethyl acetate (EA) and THF are considered as Lewis bases, which can stabilize the growing carbocations due to their nucleophilicity[30]. We were therefore interested to investigate the effect of EA on the polymerization (Table S2). We found that the polymerization behaves as expected from a living polymerization process, displaying a linear semi-logarithmic plot, suggesting constant concentration in cations during reaction (Figure 1A), ,a linear evolution of molecular weight with monomer conversion (Figure 1B) and narrow molecular weight distributions (<1.3). In addition, the SEC traces shifts to high molecular weight with conversion, although displaying tailing towards low molecular weights, indicative of the formation of a small amount of dead (Figure 1C). It is however noteworthy that molecular weights are higher than theoretical values, which may be due to the use of a polar solvent. Altogether, these date suggest a controlled cationic polymerization showing the characteristics of a living process.

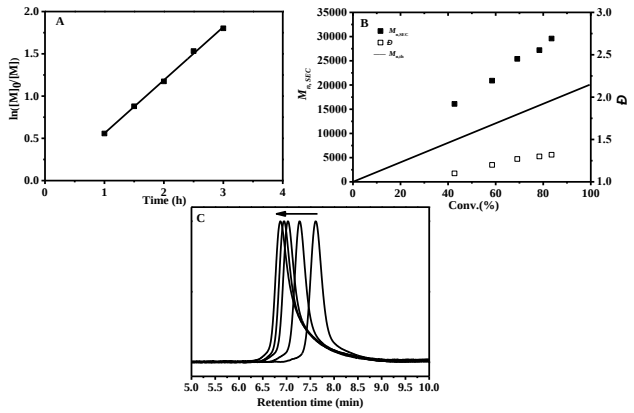


Figure 1. Polymerization results of IBVE under blue LED at 0 °C with the molar ratio $[IBVE]_0 : [EBP]_0 : [Mn_2(CO)_{10}]_0 = 200 : 1 : 0.2$, $v_{IBVE} = 0.5$ mL, $v_{EA} = 0.5$ mL, A) ln([M]$_0$/[M]) versus time; B) molecular weight (*M*n) and molecular weight distribution (*Đ*) versus conversion. C) SEC traces of PIBVE obtained in kinetic experiments.

The polymerization mechanism was further investigated by ^{1}H NMR, ^{13}C NMR and MALDI-TOF spectroscopy. ^{13}C NMR reveals the splitting of the methylene carbon in PIBVE due to stereoregularity, an observation which informs on the mechanism (radical or cationic) of the polymerization, by calculating the *meso*(*m*) diad content. From Figure 2A, the *m*-rich diad tacticity (58.8%) supports that the polymerization proceeds by a cationic mechanism, as suggested in literature[31]. The signals in ^{1}H NMR of PIBVE (Figure 2B) were also assigned according to literature,[32] to show the presence of the terminal groups of aldehyde, alkenal and β-elimination product, as well as the alkyl group from the organic halide (labeled g, f and h), which implies that the organic halide acts as a carbenium ion to form the α-end group of PIBVE. In addition, the calculated value of molecular weight from ^{1}H NMR ($M_{n,NMR}$) ($M_{n,NMR} = (2 \times (H_b + H_c)/3) \times M_{IBVE} + M_{EBP}$) assuming each polymer chain containing one EBP moiety in the chain end was 10900 g moL^{-1}, which matches well the SEC value of 11500 g mol^{-1}. The MALDI-TOF MS depicted in Figure 2C further clarifies the structure of the polymer. Two main series of peaks are observed in the spectrum, and the interval of 100.24 m/z correspond to the molar mass of IBVE unites well. The m/z values for the series with A_{48}, B_{48}, C_{48} and D_{48} respectively agrees well with the masses of the Na^+ adducts of PIBVE with the alky group at α-end and methoxy, aldehyde, alkenal and β-elimination group at ω-end. For example, series A, $n = 48$, $M_{Cal.} = 4962.69$, $M_{Found} = 4961.02$.

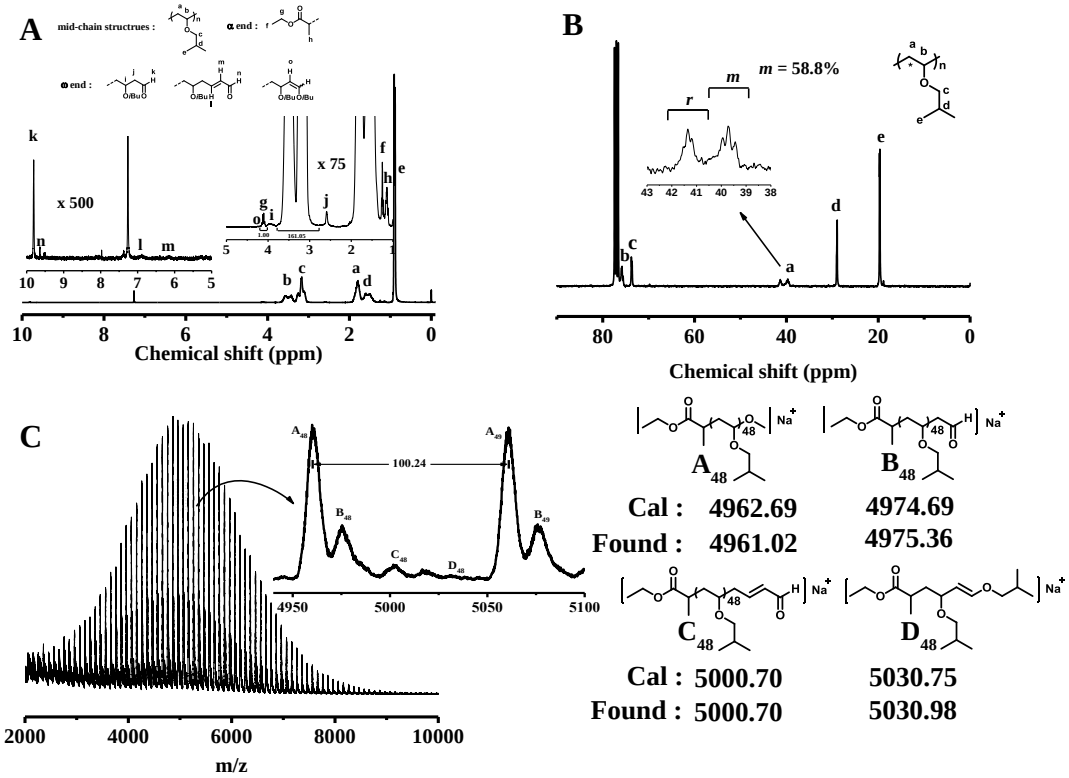
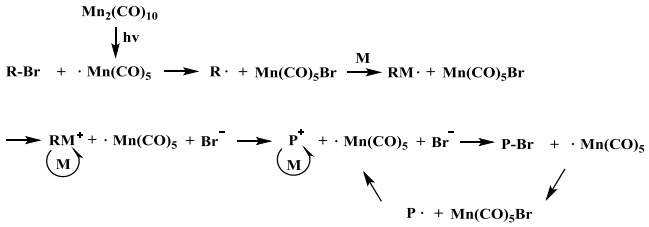


Figure 2. A) ^{13}C NMR spectrum of PIBVE ($M_{n,SEC}$ = 11500 g mol $^{-1}$, $Đ$ = 1.19, conversion = 75.5%), prepared under blue LED at 0 °C ($[IBVE]_0 : [EBP]_0 : [Mn_2(CO)_{10}]_0 = 100 : 1 : 0.2$, t = 1 h, $V_{IBVE} = 0.5$ mL, $V_{EA} = 0.5$ mL); B) ^{1}H NMR spectrum of PIBVE ($M_{n,SEC}$ = 11500 g mol $^{-1}$, $Đ$ = 1.19, conversion = 75.5%), prepared under blue LED at 0 °C ($[IBVE]_0 : [EBP]_0 : [Mn_2(CO)_{10}]_0 = 100 : 1 : 0.2$, t = 1 h, $V_{IBVE} = 0.5$ mL, $V_{EA} = 0.5$ mL); C) MALDI-TOF MS of PIBVE ($M_{n,SEC}$ = 7100 g mol $^{-1}$, $Đ$ = 1.15, conversion = 17.3%), prepared under blue LED at 0 °C ($[IBVE]_0 : [EBP]_0 : [Mn_2(CO)_{10}]_0 = 100 : 1 : 0.2$, t = 10 min, $V_{IBVE} = 0.5$ mL, $V_{EA} = 0.5$ mL).

Based on these evidence, we propose the following cationic mechanism (Scheme 2): The first step is the conventional photolysis of manganese carbonyl and halide abstraction to generate a carbon-centered radical and $Mn(CO)_5Br$. Next is a radical addition between free radicals and vinyl monomers, which formed an active vinyl ether-type radical. According to Mn-containing complexes with similar structures utilized as eletrocatalysts[33] and traditional ATRA process[1], we hypothesis

that $Mn(CO)_5Br$ can oxidize the carbon radicals to carbenium ions, after which a bromide ion is generated, together with a manganese radical, to restart the process. In this process, the organic halides are transferred to carbenium ions without consuming the Mn complex, which is consistent with the data showed in Table 1 (Entry 1-3). However, the amount of active species is affected when the amount of manganese carbonyl is too small, due to some possible side reactions, such as dimerization. Controlled polymerization is obtained by reversible termination of the propagating carbenium. Moreover, cyclic voltammetry was performed on $Mn(CO)_5Br$ to prove the oxidation process; a reduction peak at *ca.* – 1.35 V was observed (Figure S4) and the redox potential was obtained from literature[2]. To test the application of this technique for the polymerization to other monomers, ethyl vinyl ether (EVE), butyl vinyl ether (BVE) and 2-chloroethyl vinyl ether (Cl-EVE) were polymerized under the same conditions. The molecular mass distributions of poly(EVE) (Entry 1, Table S2) and poly(BVE) (Entry 2, Table S2) are slightly broader than that of PIBVE, and the polymerization rate of Cl-EVE (Entry 3, Table S2) is slightly slower. These differences show that the structure of the organic halides and monomers should be matched to btain controlled polymerization. Nevertheless, these results indicated this method is versatile and can be applied to a variety of vinyl ethers.



Scheme 2. Proposed mechanism of the polymerization.

As mentioned above, the amount of active species will be affected when the amount of manganese carbonyl is too low. On the other hand, the amount of $Mn(CO)_5Br$, and therefore the targeted molecular weight, can be modified by adjusting the irradiation time. A number of polymerizations were performed under standard condition at different irradiation times, and the results are shown in Table S3. We observed that the polymerization is not stopped by turning off the light, which indicates that the light is only essential for the initiation process, and not for the propagation step. The polymerization rate decreases as irradiation time decreases, although there is no obvious difference in molecular weights after 2 minutes of irradiation time (Entry 1-4, Table 2). Nevertheless, the molecular weight increases when further reducing irradiation time (Entry 5-6, Table 2). All these observations are consistent with our proposed mechanism above. UV-vis spectroscopy was also used to monitor the initiating process. Firstly, a calibration curve was obtained by UV/Vis absorbance of various concentrations in $Mn_2(CO)_{10}$ (Figure S7). this calibration curve was then used to follow the conversion of $Mn_2(CO)_{10}$ during reaction under blue light (Figures S8 and S9). We observed that $Mn_2(CO)_{10}$ was almost all consumed after 2 min, which is consistent with the data of entry 1-4 in table 2. The conversion of $Mn_2(CO)_{10}$ under blue light after irradiation for 20s is about 40%, see Figure S9, which indicates a molar ratio EBP : $Mn_2(CO)_{10}$ of 1 : 0.08. This data partly explained the result of entry 6 in table 2, taking into account possible errors caused by side reactions and different concentrations between testing solution and reaction solution. In addition, a light on/off experiment wa also performed. The reaction mixture was exposed to light for 20 s, followed by 20 h in the dark, foolowed by 10 minutes further irradiation. Comparing the product of this reaction to the polymer prepared under the same conditions but without a second light irradiation, a bimodal distribution was observed by SEC trace (Figure S6). We conclude that the first light irradiation consumed only part of the initiator, and the residual initiator was further consumed to reinitiate the polymerization in the following irradiation. Polydisperse polymers could therefore be prepared by adjusting the light source, thus providing a simple way to obtain a range of materials.

Finally, this method was applied to a polymeric chain exhibiting a halide chain end, which may be utilized for post polymerization, for example to prepare block copolymers. A chain extension experiment was performed from a polystyrene prepared by traditional ATRP. As shown in Figure 3, the SEC trace of the final block copolymer is shifted to higher molecular weights with a small tail at lower molecular weights, thus indicating a successful chain extension, albeit the presence of some non re-initiated chains.

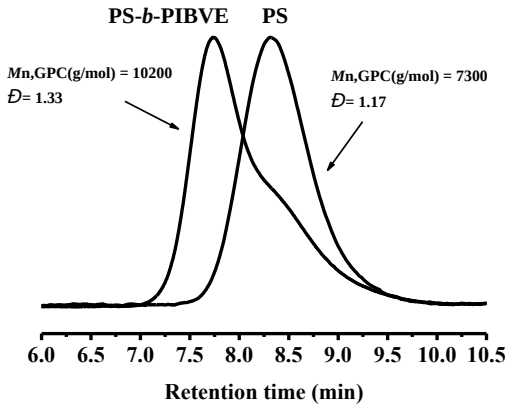


Figure 3. Chain extension with the molar ratio [IBVE] : [PS] : $[Mn_2(CO)_{10}]$ = 800 : 1 : 0.8

In conclusion, we report a new method for controlled cationic polymerization under visible light. Poly(vinyl ethers) can be easily prepared under mild condition with commercially available reagents. Moreover, polydisperse polymers can be obtained by simply adjusting the light source, which brings potential advantages for preparing novelty materials.

■ ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge via the Internet at http://pubs.acs.org."

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Notes

The authors declare no competing financial interests. # These two authors contribute equally for this manuscript.

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Visible light induced controlled cationic polymerization by in-situ generated catalyst from manganese carbonyl

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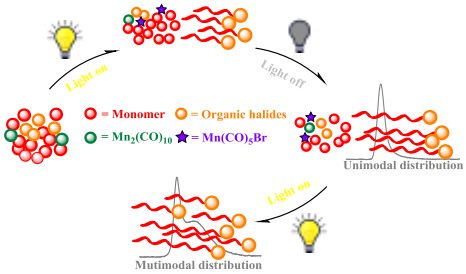

Controlled cationic polymerization of various vinyl ethers is obtained under light radiation, utilizing commercially available reagents, under mild conditions and the molecular weight distributions can be modulated by simply regulating the irradiation time of the light source.